# High-Value Synthetic Chemicals and Gasoline Drop-In Liquid Fuels From Canada's $CO_2$ and Flare Gas Emissions

## Butanol from Greenhouse Gases

### Non-Confidential Final Report

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**For:**

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This report describes work conducted at Pioneer Energy between April 10, 2014 and April 9, 2016. Dr. Robert Zubrin is the Principal Investigator for Pioneer Energy. Nevin Fleming is the Project Advisor for CCEMC.

## Introduction

This non-confidential report reviews the work done in successfully developing a functioning system to make 10 liters per day of butanol from greenhouse gases for the CCEMC Grand Challenge Project at Pioneer Energy and other important tasks necessary to advance this technology towards commercialization.

Efforts to build a strong patent portfolio for this technology (without using CCEMC funds) were successful with the grant of broad patent rights in the US. We received a favorable response and are nearing the close of prosecution and grant of our first Canadian patent while applications in other countries are moving forward. Comprehensive studies on sources of greenhouse gas feedstock with a focus on Alberta were done. Technology transfer efforts to identify partners/investors in the chemical industry were carried out. Alberta company Enerkem was identified and contacted and a preliminary agreement to collaborate for the next phase of development was reached. A market study was conducted and it identified high demand for renewable C4 chemicals like butanol in a global industrial chemicals market that is over $6.5 billion CAN for 1-butanol and about $3.5 billion CAN for 2-butanol.

The CCEMC-Pioneer Butanol from Greenhouse Gas (BFGG) process converts methane and carbon dioxide to butanol. The key process steps include methanol synthesis via production of syngas from flared gas or other methane sources, acetic acid synthesis by carbonylation of methanol using carbon monoxide produced from carbon dioxide via the reverse water gas shift (RWGS) reaction, ketene synthesis from acetic acid, diketene production via dimerization of ketene, preparation of methyl acetoacetate (MAA) from diketene and recycled methanol, and finally hydrogenation of MAA to generate butanol product. The methanol synthesis and acetic acid production technologies are well-established. The conversion of carbon dioxide to carbon monoxide to supplement syngas production via the reverse water gas shift (RWGS) reaction has been successfully implemented by Pioneer in previous aerospace applications. Therefore, the focus of the CCEMC Phase A and Phase B efforts was on the downstream production of ketene and diketene followed by hydrogenation to produce butanol.

## Process Development from Lab scale to 10L Butanol/day

A project management plan consisting of a work breakdown structure and supporting narrative that addressed the overall project including technology transfer efforts was prepared. The process goal for the first year (Phase A) was to have a functioning system producing butanol at a nominal 1 L/day rate. The process was scaled up to produce butanol at the rate of 10 L/day by the end of the second year (Phase B).

The Phase A System was designed, and hardware components including steel tubing, fittings, valves, instruments, thermocouples, gauges, chemicals including catalysts were ordered and the reactors were fabricated and set up in fume hoods.

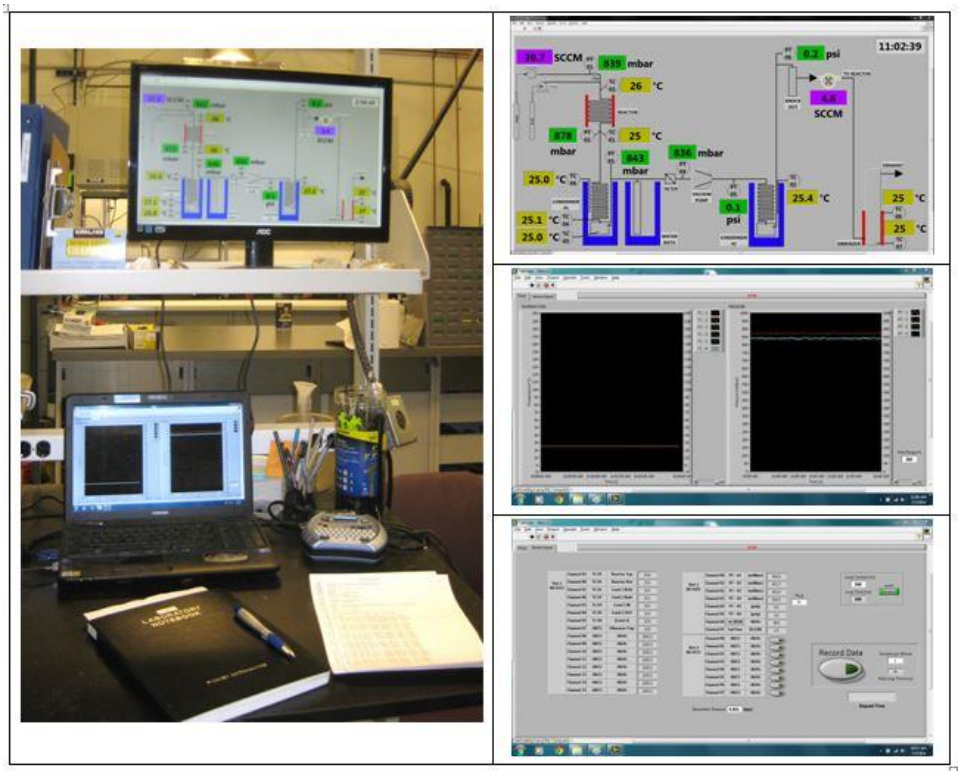
Analytical methods for the Butanol from Greenhouse Gases process were developed to support the experimental effort and process development. A gas chromatograph-mass spectrometer (GC-MS) consisting of a Hewlett Packard 6890 series gas chromatograph coupled to an Agilent 5973 mass selective detector was used for analysis of liquid and gas streams. In addition, an Agilent CP-4900 four-channel micro GC was used for quick analysis of gas samples. A Gow-Mac 580 GC was to analyze liquid samples. The GC-MS and micro GC provided the majority of the required gas and liquid analyses. The Gow-Mac GC was used for analysis of water from the condensers indicating conversion rate of acetic acid to ketene and water product as an alternate method to confirm other analyses.

The ketene synthesis and diketene production modules were assembled as single unit operated in a dedicated fume hood. The hardware was placed in an expanded layout to allow room for flow sheet revisions and hardware modifications as the experimental program progressed.

The reactor system design consists of three main parts which are, a) Ketene Synthesis Reactor b) Ketene Absorber and Dimerizer, and c) Hydrogenation Reactor. The ketene reactor was designed to be compact and fit in a large hood but easily amenable to modifications as experimental results required them.

A Ketene Absorber/Dimerizer system was designed and built so that ketene gas could be absorbed in diketene liquid. The resulting solution of dissolved ketene was warmed and circulated to allow time for dimerization to diketene.

The synthesis of ketene/diketene via catalytic decomposition of acetic acid was shown to take place at high conversion and selectivity in a process amenable to scale up to commercial rates. The laboratory hardware and materials of construction were demonstrated to be resilient to the operating conditions and chemicals.




**Ketene synthesis data acquisition and control displays.**


**Phase A ketene/diketene production apparatus.**

**Agilent GCMS system for analysis of condensates and products.**

The Phase B, 10 L/day ketene/diketene reactor system was designed and scaled based on results of Phase A experiments. Acetic acid conversions were in line with those reported in industry.

The Phase A hydrogenation system for butanol synthesis designed to be compact yet easily modified was fabricated and assembled in a separate fume hood. After calibrations and testing of the subsystems, catalyst was loaded and reactions were commenced.

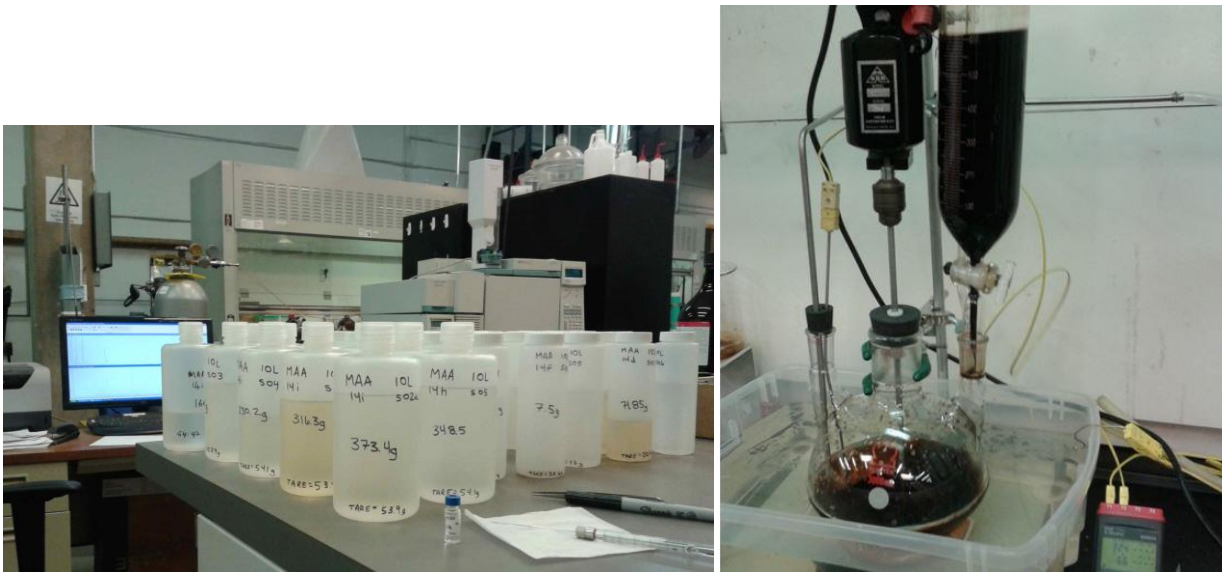
A number of exploratory experiments were conducted to screen catalysts and key conditions including temperature, pressure, retention time, and hydrogen:diketene ratio. Early results showed that with optimization (catalyst, temperature, pressure, hydrogen ratio), a total of about 85 percent alcohol yield (predominately butanol) can be achieved by hydrogenation of the crude diketene produced at Pioneer.

During the course of hydrogenation experiments and process evaluation, additional potentially favorable reaction pathways for conversion of diketene to butanol were identified. The preferred pathway involves production of methyl acetoacetate (MAA) an important industrial chemical produced from diketene and methanol followed by hydrogenation of MAA to form butanol and methanol. The methanol is recirculated to react with another batch of diketene and is thus not consumed.

Experiments were conducted at Pioneer to verify the production of MAA. Methyl acetoacetate was subjected to hydrogenation in the reactor system described above yielding positive results producing butanol as the major product with methanol and water along with some byproduct propanol and only a small amount of unreacted ester/ketone formation. Diligent efforts were put in as experimental conditions were sought to maximize butanol yields. Dozens of reactions were performed to optimize the reaction conditions yielding efficient conversions to butanol under modest temperature and pressure conditions with excellent catalyst longevity.

The Phase B reactor system was designed for scale up to 10 L/day butanol with inclusion of a catalyst bed containing a cooling system to control the temperature rise due to exothermic nature of hydrogenation. Running the hydrogenation system at the full 10L/day yielded excellent results corresponding to those observed on smaller scale.

**Final Phase B hydrogenation reactor system.**




**Product samples from hydrogenation experiments (left)** and **MAA synthesis from diketene (right)**.

The hydrogenation step to form butanol has been demonstrated in the laboratory at 10L/day using conditions that employ moderate temperature and pressures using inexpensive commercial copper based catalyst that would have excellent longevity and economic value for the process.

In conclusion, unit operations of Pioneer's Butanol from Greenhouse Gases process developed during Phase 1 were demonstrated at a laboratory scale and successfully scaled to rates supporting production of 10 liters per day of butanol. Important process parameters were identified during the course of the Round 1 effort, and through laboratory and demonstration experiments, a design basis for further scale up was established in support of a proposed Round 2 effort at much larger scale.

## Technology Transfer Overview

Research was conducted, and a list of potential partners, investors or companies that would be interested in licensing this technology was compiled. A market study of butanol and its commercial uses as an important industrial chemical was conducted.

Contacts were made with companies that are operating in the acetyl chemicals sector and that can easily integrate this technology into their manufacturing. Contacts were made and discussions and agreements were reached. Academic presentations were made at academic conferences, and academic papers were accepted for publication, which advances the goal of widespread dissemination of the scientific and technical knowledge gained during this research. One academic presentation was conducted at the Carbon Capture, Utilization and Storage Conference (CCUS) in 2014 in Pittsburgh, PA. Expedited patent applications were filed and our first U.S. Patent 8,927,789 for Pioneer Energy's butanol technology was granted in January 2015. Following this, US Patents 9,040,757 and 9,080,119 were granted as of mid-2016 and other applications continue to complete prosecution successfully and be issued for Pioneer Energy's ketene technology. Our Canadian application is expected to be granted in 2016. Patent applications were also filed in India, China, Australia, and New Zealand.

## $CO_2$ Lifecycle Emissions Modeling

Data were collected on the process $CO_2$ emissions. The process life cycle $CO_2$ emissions were modeled and analyzed to predict the total process emissions reduction relative to petroleum based gasoline. Results were used to compare the process to other alternative butanol production processes and to determine its environmental benefits for $CO_2$ mitigation. In addition, a market study on butanol and its uses was conducted, both as a fuel and industrial chemical, to understand total market GHG reduction potential in Alberta. The analysis of the base case of $CH_4$ from flare gas and $CO_2$ from a stationary source showed a $CO_2$ footprint of 11.4 g CO2e/MJ butanol, representing a reduction of 87% relative to an average Alberta gasoline emission factor of 90.1 g CO2e/MJ. When $CH_4$ from a natural gas pipeline and $CO_2$ from a stationary source are used in the process, the net $CO_2$ footprint was estimated to be 65.4 g CO2e/MJ butanol, which still represents a 27% reduction relative to average Alberta gasoline. Finally, if $CH_4$ from a biogas source, such as a landfill or livestock manure operation, is utilized, the net $CO_2$ footprint is reduced to 7.0 gCO2e/MJ butanol, representing a 92% reduction relative to average Alberta gasoline and approaching completely carbon-neutral operations. A single 38 million Liter/year (10M gal/year) butanol plant would reduce emissions in Alberta by 0.31 Mt CO2e/year (Megatons) if operating on flare gas and $CO_2$, 0.10 Mt CO2e/year if operating on commercial natural gas and $CO_2$, and 0.33 Mt $CO_2$e/year if operating on biogas and $CO_2$. Therefore, an emission reduction of 1 Mt $CO_2$/year can be achieved in Alberta from just 3-10 butanol plants depending on the feedstock, assuming a plant size of just 38 million liters. As a point of reference, Enekem's plant located in Edmonton, Alberta produces about 38 million Liters of biomethanol from municipal solid waste.

## Lifecycle GHG Inventory Results

The results of the lifecycle $CO_2$ emissions analysis are shown in the table below

### Lifecycle $CO_2$ Emissions Results

| | **Net reaction: $3CH_4 + CO_2 \rightarrow C_4H_9OH + H_2O$** | | |
|---|---|---|---|
| **Per 1.00 kg Butanol** | **Butanol from Flare Gas and $CO_2$** | **Butanol from Pipeline Natural Gas and $CO_2$** | **Butanol from Landfill Biogas ($CH_4$) and $CO_2$** |
| **$CH_4$ Feedstock consumed (kg $CH_4$/kg butanol)** | 0.65 | 0.65 | 0.65 |
| **$CO_2$ Feedstock consumed (kg $CO_2$/kg butanol)** | 0.59 | 0.59 | 0.59 |
| **Feedstock ($CH_4$+$CO_2$) consumed (kg GHG/kg butanol)** | 1.24 | 1.24 | 1.24 |
| **Water ($H_2O$) generated** | 0.24 | 0.24 | 0.24 |
| **Butanol produced (Mass balance verification)** | 1.00 | 1.00 | 1.00 |
| | | | |
| **Lifecycle emissions (kg $CO_2$e/kg butanol):** | | | |
| *(1) $CH_4$ Upstream Emissions or Emission Reductions* | -2.16 | 0.003 | -2.16 |
| *(2) $CH_4$ Pre-Processing* | 0.00 | 0.00 | 0.00 |
| *(3) $CH_4$ Transport to Central Butanol Plant* | 0.31 | 0.00 | 0.15 |
| *(4) $CO_2$ Capture from Stationary Source* | -0.65 | -0.65 | -0.65 |
| *(5) $CO_2$ Transport to Central Butanol Plant* | 0.001 | 0.001 | 0.001 |
| *(6) Central Butanol Plant Conversion* | 0.51 | 0.51 | 0.51 |
| *(7) Butanol Product Transport* | 0.000 | 0.000 | 0.000 |
| *(8) Butanol Product Combustion/Utilization* | 2.38 | 2.38 | 2.38 |
| **Total (kg $CO_2$e/kg butanol)** | 0.39 | 2.25 | 0.24 |
| | | | |
| **Total (g $CO_2$e/MJ, LHV)** | **11.4** | **65.4** | **7.0** |
| **% Reduction Relative to Alberta Gasoline** | **87%** | **27%** | **92%** |

In conclusion, the analysis of the base case of $CH_4$ from flare gas and $CO_2$ from a stationary source showed a significant $CO_2$ reduction potential (87%) relative to Alberta average gasoline. When $CH_4$ from a natural

gas pipeline and $CO_2$ from a stationary source is used in the process, the net $CO_2$ footprint still represents a meaningful reduction (27%) relative to average Alberta gasoline. Finally, if $CH_4$ from a biogas source, such as a landfill or livestock manure operation, is utilized, the net $CO_2$ footprint approaches completely carbon-neutral operations (a 92% reduction relative to average Alberta gasoline). There is sufficient market in both the world butanol demand, and the Alberta specific gasoline demand, to accept all of the butanol product produced, considered as either a chemical commodity or a transportation fuel. Therefore, achieving an emission reduction of 1 Mt/year in Alberta is achievable with this technology and is expected to meet the CCEMC carbon emission reduction targets.

## Alberta Applicability and Economics Study by McMaster University

A study was conducted to develop a model and analyze collected data to determine the optimal strategy for the determination of a flare gas-to-butanol supply chain incorporating the PERT-2 modular methanol production system being developed by Pioneer Energy.

Key conclusions of the McMaster study are as follows:

- Under the base case market conditions, the most profitable routes used methanol from a traditional gas-to-methanol process with pipeline natural gas, but with negligible environmental benefit.
- Routes that reduce $CO_2$ emissions the most are ones that use as much flare gas as possible via the hypothetical improved PERT-2 device, but this is unprofitable.
- Routes which used a mixture of both flare gas and pipeline natural gas to produce methanol were found to have environmental benefit in the form of avoided $CO_2$ emissions and still be profitable.

## Project Costs

Pioneer Energy commenced work on the CCEMC Grand Challenge project in April 2014 after receipt of the $500,000 grant and work continued for two years until April 2016. At the conclusion of the Round 1 CCEMC Grand Challenge project, Pioneer Energy spent a total of $753,716 (CAD). As seen in the tables below, Pioneer Energy spent $257,310 over the CCEMC grant funds to ensure expedient progress of Pioneer's butanol technology.

The following tables summarize project revenues and expenditures for the life of the project.

| Revenues | |
|---|---|
| **Description** | Amount |
| **CCEMC** | $500,000 |
| **Pioneer Energy** | $257,310 |
| **Total** | $757,310 |

| Expenditures | | |
|---|---|---|
| **Description** | Budget | Actual Amount Spent |
| **Salaries & Benefits** | $390,000 | $616,935 |
| **Supplies** | $23,542 | $27,653 |
| **Travel** | n/a | n/a |

| | | |
|---|---|---|
| **Capital** | n/a | n/a |
| **Sub-Contractor-McMaster University** | $20,000 | $25,597 |
| **Other-General Administrative** | $66,458 | $87,124 |
| **Total** | $500,000 | $757,310 |

## Conclusion

The CCEMC Grand Challenge Round 1 Butanol from Greenhouse Gases program laid a strong foundation for further development and scale up of Pioneer's novel process to produce valuable renewable fuels and chemicals. Pioneer was invited to submit a proposal for Round 2 in which a fully integrated mini-pilot demonstration system will be built and operated. Pioneer will perform further scale up to large demonstration and then commercial scale systems. These efforts are expected to be planned as project development progresses and implemented as quickly as possible after evaluating results.